

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

Hawtof 8-1-1

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

60/095,735 09/762274

INTERNATIONAL APPLICATION NO.

PCT/US99/16176

INTERNATIONAL FILING DATE

16 July 1999

PRIORITY DATE CLAIMED

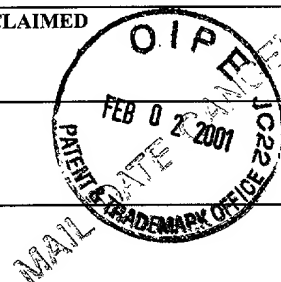
7 August 1998

TITLE OF INVENTION

CREATING SILICA SOOT WITH A PLUG-FREE SYSTEM

APPLICANT(S) FOR DO/EO/US

Corning Incorporated



Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19<sup>th</sup> month from the earliest claimed priority date.
5. ☐ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. To 16. Below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An Assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

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17. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a)(1)-(5):**

Search Report has been prepared by the EPO or JPO.....\$840.00  
 International preliminary examination fee paid to USPTO (37 CFR 1.482).....\$670.00  
 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but  
 international search fee paid to USPTO (37 CFR 1.445(a)(2)).....\$760.00  
 Neither international preliminary examination fee (37 CFR 1.482) nor international search  
 fee (37 CFR 1.445(a)(2)) paid to USPTO.....\$970.00  
 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims  
 satisfied provisions of PCT Article 33(2)-(4).....\$96.00

**CALCULATIONS PTO USE ONLY****ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 96.00**

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from  
 the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	31 - 20 =	11	X \$18.00
Independent claims	3 - 3 =	0	X \$78.00
MULTIPLE DEPENDANT CLAIM(S) (if applicable)			+ \$260.00

\$ 198.00

\$

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**TOTAL OF ABOVE CALCULATIONS = \$ 294.00**

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity  
 Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28)

\$

**SUBTOTAL = \$ 294.00**

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
 months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

**TOTAL NATIONAL FEE = \$ 294.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property

\$ 40.00

**TOTAL FEES ENCLOSED = \$ 334.00**

**Amount to be  
 refunded:**

\$

**Charged: \$ 334.00**

- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Corning Incorporated hereby authorizes use of Deposit Account No. 03-3325 in the amount of  
**\$ Error! Reference source not found.** to cover the above fees. A duplicate copy of this sheet is  
 enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or  
 credit any overpayment to Deposit Account No. 03-3325. A duplicate copy of this sheet is enclosed.
- NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

Send all correspondence to:

Timothy R. Krogh  
 Corning Incorporated  
 SP-TI-03  
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Signature

Timothy R. Krogh

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Date: 2-1-01

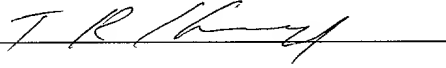
09/762274

JC03 Rec'd PCT/PTO 01 FEB 2001  
Attorney Docket No.: Hawtof 8-1-1

CERTIFICATE OF EXPRESS MAIL UNDER 37 CFR 1.10:

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on 2-1-01 above and is Addressed to the Commissioner of Patents and Trademarks, Washington, DC 20231

Signature



"EXPRESS MAIL" Mailing Label No.

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

**Applicant(s):** Daniel W. Hawtof et al.

PRELIMINARY AMENDMENT

**Serial No.:****Filing Date:**

Group Art Unit: TBA

**Title:** CREATING SILICA  
SOOT WITH A PLUG-  
FREE SYSTEM

Examiner: TBA

Assistant Commissioner for Patents  
Patent and Trademark Office  
Washington, DC 20231

Sir:

**PRELIMINARY AMENDMENT**

Prior to examination of the above captioned application and issuing a first office action on the merits, please enter this amendment, as set forth below.

**IN THE CLAIMS**

Please add new claims 26-31.

26. A method of forming soot for use in the manufacture of glass comprising:

- a) selectively delivering a preselected liquid from a group of liquids consisting of a liquid reactant or a second liquid to a combustion zone through a common conduit, wherein an atmosphere exposed to the combustion zone comprises an atmosphere of water contained in air ;
- b) changing from delivering the preselected liquid to the combustion zone to delivering the liquid not delivered during said step a) to the combustion zone, wherein said the liquid not delivered during said step a) is selected from the group of liquids consisting of the liquid reactant and the second liquid; and
- c) reacting said liquid reactant in said combustion zone to form the soot.

27. The method according to claim 26 wherein the second liquid comprises a halide-free liquid.
28. The method according to claim 26 wherein step b) comprises the step of simultaneously decreasing the flow of the liquid reactant and increasing the flow of the second liquid.
29. The method according to claim 26 wherein step b) comprises the step of simultaneously increasing the flow of the liquid reactant and decreasing the flow of the second liquid.
30. The method according to claim 26 wherein said step b) occurs during a steady state of liquid flow into the combustion zone.
31. The method according to claim 1 wherein an atmosphere exposed to the combustion zone comprises an atmosphere of water contained in air.

#### **REMARKS**

The claims pending in the application are claims 1-31. In the amendment, the applicants have added new claims 26-31 to the application. In addition, the applicants submit that no new matter has been added to the application as a result of the inclusion claims 26-31. Consideration and entry of the amendment to the claims is respectfully requested.

**CONCLUSION**

The applicants respectfully request a first action on the merits with respect to claims 1-31 of the application, as amended above. Should the Examiner have any questions or comments regarding the invention, or this amendment, he is courteously invited to contact the undersigned attorney at the address and telephone number listed below.

Respectfully submitted,

DATE:

TRK/bab

Date of Deposit: 2-1-01

I hereby certify that this paper (along with any paper referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date indicated above with sufficient postage as first class mail in an envelope addressed to the: Commissioner of Patents and Trademarks, Washington, DC 20231

Signature

Timothy R. Krogh  
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09/762274

PCT 1 FEB 2001

CREATING SILICA SOOT WITH A PLUG-FREE SYSTEM

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FIELD OF THE INVENTION

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The present invention relates to the delivery of liquid reactants to a combustion zone formed adjacent a burner assembly to create soot used in the manufacture of glass. More particularly, the present invention relates to a system and method of delivering liquid reactants to a combustion zone that avoids the premature solidification of the liquid reactants within the burner assembly.

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While the invention is subject to a wide range of glass soot deposition applications, it is especially suited for use in producing soot for glass preforms used in the manufacture of optical waveguides, and will be particularly described in that connection.

BACKGROUND OF THE INVENTION

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Various processes are known in the art that involve the production of metal oxides from vaporous reactants. Such processes require a feedstock solution or precursor, a means of generating and transporting vapors of the feedstock solution (hereafter called vaporous reactants) and an oxidant to a conversion reaction site (also known as a soot reaction zone or combustion

zone to those skilled in the art), and a means of catalyzing oxidation and combustion coincidentally to produce finely divided, spherical aggregates, called soot. This soot can be collected in any number of ways, ranging from capture in a collection chamber to deposition on a rotating mandrel. The collected soot may be simultaneously or subsequently heat treated to form a non-porous, transparent, high purity glass article. This process is usually carried out with specialized equipment having a unique arrangement of nozzles, injectors, burners and/or burner assemblies.

Much of the initial research that led to the development of such processes focused on the production of bulk silica. Selection of the appropriate feedstock was an important aspect of that work. Consequently, it was at that time determined that a material capable of generating a vapor pressure of between 200-300 millimeters of mercury (mm Hg) at temperatures below approximately 100°C would be useful for making such bulk silica. The high vapor pressure of silicon tetrachloride ( $\text{SiCl}_4$ ) suggested its usefulness as a convenient vapor source for soot generation and launched the discovery and use of a series of similar chloride-based feedstocks. This factor, more than any other is responsible for the presently accepted use of  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{POCl}_3$ , and  $\text{BCl}_3$  as feedstock vapor sources.

Use of these and other halide-based feedstocks as vapor sources, however, does have its drawbacks. The predominate drawback being the formation of hydrochloric acid (HCl) as a by-product of oxidation. HCl is not only detrimental to the deposition substrates and the reaction equipment, but to the environment as well. Overcoming this drawback, amongst others, led to the use of halide-free compounds as precursors or feedstocks for the production of soot for optical waveguides.

Although use of halide-free silicon compounds as feedstocks for fused silica glass production, as described in U.S. Patent Nos. 5,043,002 and 5,152,819, for example, avoids the formation of HCl, other problems remain, particularly when the soot is intended for the formation of optical waveguides. It has been found that, in the course of delivering a vaporized polyalkylsiloxane to the burner, high molecular weight species can be deposited as gels in the



lines carrying the vaporous reactants to the burner, or within the burner itself. This leads to a reduction in the deposition rate of the soot that is subsequently consolidated to a blank from which an optical waveguide fiber is drawn. It also leads to imperfections in the blank that often produce defective and/or unusable optical waveguide fiber from the effected portions of the blank. An additional problem encountered while forming silica soot using siloxane feedstocks is the deposition of particulates having high molecular weights and high boiling points on the optical waveguide fiber blank. The build-up of these particulates results in "defect" or "clustered defect" imperfections that adversely affect the optical and structural quality of optical waveguides formed using the silica soot.

Other feedstocks, some of which are, and others of which may be useful in forming soot for the manufacture of optical waveguides are not currently acceptable alternatives to the halide-based and halide-free feedstocks for delivery via vapor deposition. Materials such as salts and those known as rare-earth elements, for example, are extremely unstable as vapors and often decompose before they can be delivered in their vapor phase, or do not have sufficiently high vapor pressures to be vaporized at accessible temperatures.

Although it is often possible to deliver at least a percentage of these elements to the combustion zone as a vapor, it is technically very difficult. Elaborate systems incorporating expensive equipment are necessary to convert these elements to the vapor phase, and further, to deliver them to the combustion zone without leaving deposits in the lines leading to the burners and in the burners themselves. Moreover, if multiple elements are being delivered as vapors and a specific percentage of each is needed for the desired composition, it is difficult to control the delivery since different elements have different vapor pressures.

U.S. Patent Application Serial Number 08/767,653, discloses that these and other limitations can be overcome by delivering a feedstock to an injector or burner in liquid form, atomizing the feedstock to form an aerosol containing fine droplets of the liquid feedstock, and converting the atomized liquid feedstock into soot at the combustion zone. Because the feedstock is

delivered directly into the burner flame as a liquid rather than a vapor, the vapor pressure of the feedstock is no longer a limiting factor in the formation of soot for use in the manufacture of optical waveguides. The injectors, burners, and burner assemblies disclosed in U.S. Patent Application Serial Number 08/767,653 and other currently pending applications rely on very small orifices to deliver the liquid in a fine stream for proper atomization. Because the orifices are so small, they are extremely susceptible to plugging. Even a small solid particle in the liquid being delivered can partially clog the orifice, which in turn adversely effects the soot deposition rate, and the homogeneity of the soot collected.

Although materials never before delivered to a combustion zone to form soot for the manufacture of glass can now be delivered in a liquid solution, many of these materials have inherent short-comings while in a liquid form. Most problematic is that many of these liquid materials quickly form solids when exposed to oxygen and/or water. Thus, any exposure to the air during liquid delivery of these reactants likely will result in the formation of solids, which clog the lines leading to the burners and the small orifices of the burners and the burner assemblies themselves. When the orifices become partially clogged, the flame, and thus the soot stream becomes non-uniform and the soot deposition rate suffers. As a result, the liquid delivery system must be shut down so that it can be cleaned. Such cleaning operations typically require partial disassembly of the burner assembly, which results in significant production down time.

In liquid delivery systems, plugging or clogging of the burner assembly orifices is particularly problematic during the start up and shut down stages of the liquid delivery cycle. During these periods, the liquid reactant tends to trickle or sputter out of the injector orifice. This occurs during the start up stage of the liquid delivery cycle before steady state pressure is available, and at the shut down stage of the liquid delivery cycle after steady state pressure is no longer available. These limited pressure stages result in significantly reduced liquid flow rates, which in turn can provide the exposure time necessary for the slow moving liquid to react with the air to form solids. Alternatively, these liquid

feedstocks can leak and solidify on the burner face or within the burner head cavity, resulting in increased down time for cleaning or unclogging the burner. Because the liquid feedstocks can react with water in the air almost instantaneously, any amount of slow moving liquid feedstock within the injector or at the injector orifice can result in deposit of solids. The resultant partial plugging degrades burner performance for rate and quality of the soot produced, and complete plugging will stop soot deposition altogether.

There is a need therefore, for a system and method of delivering liquid feedstocks or precursors (hereinafter, "liquid reactants") through a burner assembly to form soot for the manufacture of glass that eliminates the premature solidification of the liquid reactants and therefore the plugging of burner assemblies in liquid delivery systems.

#### SUMMARY OF THE INVENTION

The present invention is directed to a system and method for delivering liquid reactants to a combustion zone adjacent a burner assembly of a liquid delivery system to produce soot for use in the manufacture of glass. In a liquid delivery system, the liquid reactant, capable of being converted by thermal oxidative decomposition to glass, is introduced directly into the combustion zone of a combustion burner; thereby forming finely divided amorphous soot. The amorphous soot is typically deposited on a receptor surface where, either substantially simultaneously with or subsequent to its deposition, the soot is consolidated into a body of fused glass. The body of glass may then be either used to make products directly from the fused body, or the fused body may be further treated, e.g., by forming an optical waveguide such as by drawing to make optical waveguide fiber as further described in, for example, U.S. Patent Application No. 08/574,961 entitled, "Method for Purifying Polyalkylsiloxanes and the Resulting Products", the specification of which is hereby incorporated by reference.

One advantage of the present invention is that the system and method facilitates against "plugging" of the burner assembly orifices and the respective

liquid delivery lines feeding those burner assembly orifices. The terms, "plugging" and "plug", as used herein, refer to the effect of solids (formed by the chemical reactions that result from exposing liquid reactants to water, and specifically, water contained in air) that collect on the inner surfaces of the lines leading to the burner assembly and walls of the burner assembly orifices. The collected solids impede or partially impede liquid flow. The system and method of the present invention are particularly well suited for eliminating plugging, and particularly, plugging that typically occurs during periods of transient liquid flow. As used herein, the phrases, "periods of transient liquid flow" and "transient liquid flow conditions" are defined as those times or periods when liquid flow is being increased to achieve steady state flow within the system. Transient liquid flow also includes these times or periods when liquid flow is being decreased from steady state liquid flow and those times or periods when liquid flow is maintained at a rate less than the selected steady state flow rate for soot deposition.

The liquid reactant preferably is prevented from being exposed to air, and thus water contained within air, during periods when the liquid reactant is not being delivered to the combustion zone to form soot. Accordingly, another advantage of the present invention is that elements previously not capable of being delivered as precursors for the formation of soot used to manufacturing glass are now capable of being delivered to form soot having qualities and properties heretofore unknown in the art. Since the liquid reactant does not come in contact with water until desired, and since the liquid precursor is not delivered as a vapor prior to its exposure to the combustion zone, elements selected from groups IA, IIA, IIIA, IIIB, IVA, IVB, VA, VB and the rare earth series of the periodic table of elements are now available to be converted by oxidation or flame-hydrolysis to soot for use in the manufacture of glass preforms.

When soot is being deposited and during other periods of steady state liquid flow, plugging is not generally a concern as the liquid enters the combustion zone before it has time to solidify enroute. However, during transient liquid flow conditions, particularly those times when liquid delivery is

started and stopped, the liquid reactant flow rate is greatly reduced and the liquid reactant tends to trickle or sputter out of the liquid exit orifice of the burner assembly. During these conditions, the liquid reactant is available within the lines and within the liquid exit orifice of the burner assembly for reaction to a solid. These solids plug the orifice as well as the lines, and therefore adversely effect the soot deposition rate.

The present invention, however, delivers an evaporative liquid through the lines and burner assembly liquid exit orifice during the transient liquid flow conditions thus removing the liquid reactant from the lines and orifice during periods of reduced liquid flow rate. Because there is no liquid reactant available in the lines and orifice during this time, only the evaporative liquid is available to trickle and sputter. The evaporative liquid simply vaporizes and evaporates from the lines and orifice without leaving behind significant solids to plug the burner assembly.

To achieve these and other advantages, the system of the present invention delivers an evaporative liquid to a combustion zone through a conduit and an injector. Flow through the conduit is selectively controlled and is transitioned from the evaporative liquid to a liquid reactant. The liquid reactant is then delivered to the combustion zone through the conduit and the injector to create soot for use in the manufacture of glass. During this transitioning, a steady state flow of liquid is maintained within the conduit leading to the combustion zone. This can be achieved for example, by first delivering evaporative liquid through the conduit until a flow rate of the evaporative liquid is established which is effective to propel a uniform flow of the evaporative liquid through the conduit and burner assembly without sputtering, or dripping on or in the burner assembly, etc. Consequently, when the flow of liquid reactant is first initiated, a continuous flow rate has already been established within the conduit (i.e., by the evaporative liquid). Moreover, even though a relatively small flow rate of liquid reactant is initially present, the method of the present invention enables the liquid reactant to be propelled through the conduit at a higher speed than would otherwise occur without the aid of the evaporative liquid. When necessary, flow can be transitioned from the liquid

reactant back to the evaporative liquid to purge the conduit and injector prior to terminating liquid flow to the combustion zone.

In another aspect, the invention includes a burner assembly for delivering a liquid reactant directly into a combustion zone as an aerosol to create soot for the manufacture of glass, and a dry environment positioned upstream from the burner assembly to house the liquid reactant. A conduit extending from the dry environment to the burner assembly carries the liquid reactant to the combustion zone via a flow control apparatus.

In yet another aspect, an inert gas is introduced into an enclosure to create a dry environment where a liquid reactant is staged. The enclosure includes a conduit for selectively transporting the liquid reactant to a combustion zone through an injector. An evaporative liquid is delivered through the conduit to the combustion zone and thereafter, the evaporative liquid is transitioned to the liquid reactant. The reactant is then delivered to the combustion zone through the conduit and the injector to form soot used in the manufacture of glass. The liquid reactant may then be transitioned to the evaporative liquid, and the evaporative liquid delivered to the combustion zone through the conduit and the injector to purge the system.

Additional features and advantages of the invention will be set forth in the detailed description, which follows, and in part will be apparent from the description, or may be learned by practice of the invention. It will be understood by those skilled in the art that both the foregoing general description and the following detailed description are exemplary and explanatory in nature and are intended to provide further explanation of the invention as claimed.

The accompanying drawings are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate several embodiments of the invention and together with the description serve to explain the principles of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 schematically depicts a first preferred embodiment of the system of the present invention.

FIG. 2 schematically depicts a second preferred embodiment of the system of the present invention.

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### DETAILED DESCRIPTION OF THE PERFERRED EMBODIMENTS

10 A number of soot collection and soot deposition techniques are employed in the manufacture of glass products. While the present invention is capable of being employed in a number of these techniques, it is particularly well suited for those techniques used to deposit soot on a target to form glass preforms used in the manufacture of optical waveguides, and specifically optical waveguide fibers. During the manufacture of optical waveguide fibers, soot typically is uniformly deposited on or within a target. The collected soot is  
15 consolidated into a high purity glass preform and thereafter subjected to further processing steps such as drawing to form a thin fiber capable of carrying and directing light. Accordingly, the present invention will be described in this regard. It will be understood by those skilled in the optical waveguide fiber art, however, that there are other systems and variations of the depicted systems in which the present invention can be incorporated to perform the functions  
20 described and claimed herein. Reference will now be made in detail to the present preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings.

25 A first preferred embodiment of the system for delivering a liquid reactant into a combustion zone to form soot for use in the manufacture of glass is depicted in FIG. 1. The liquid reactant delivery system 10 includes a burner assembly 12 incorporating injector 14 which is capable of delivering liquids to a combustion zone 16 in the form of atomized liquid droplets 18. Burner assembly 12 is preferably an atomizing burner assembly such as a  
30 burner assembly disclosed in U.S. Patent Application Serial No. 08/767,653, filed December 17, 1996, and entitled "Method and Apparatus for Forming Fused Silica by Combustion of Liquid Reactants"; U.S. Patent Application

Serial No. 08/903,501, filed July 30, 1997, entitled "Method for Forming Silica by Combustion of Liquid Reactants Using Oxygen"; U.S. Patent Application Serial No. 09/089,869, filed June 3, 1998, entitled "Method and Apparatus for Forming Silica by Combustion of Liquid Reactants Using a Heater"; U.S. Provisional Application Serial No. 60/068,255, filed December 19, 1997, entitled "Burner and Method for Producing Metal Oxide Soot"; and U.S. Provisional Application entitled "Method and Apparatus for Forming Soot for the Manufacture of Glass", filed July 31, 1998, the specifications of which are hereby incorporated by reference. However, it will be understood by those skilled in the art that other burner assemblies capable of delivering liquid reactants to a combustion zone in liquid form can be incorporated into the system of the present invention.

Liquid reactant delivery system 10 further includes a liquid reactant 30 and an evaporative liquid 34 capable of being selectively fed to injector 14 of burner assembly 12 through conduit 20. The term "liquid reactant," as used herein means any reactant capable of reacting in a combustion zone to form soot. In a preferred embodiment, the liquid reactant is a glass precursor capable of making glass soot used to manufacture preforms for optical waveguide fibers. Likewise, the term "evaporative liquid," as used herein is defined as a liquid, other than water, capable of evaporating without leaving significant solids behind. Typically, liquid reactant 30 and evaporative liquid 34 are stored in liquid reactant reservoir 28 and evaporative liquid reservoir 32, respectively. Flow control mechanism 26, preferably a 3-way valve, provides selective control of the liquid delivered to conduit 20. The desired quantities of the selected liquid are delivered to injector 14 with a conventional pump 24 and flow meter 22.

In operation, combustion reactants (not shown) are delivered through burner assembly 12 and ignited to form a flame 16 at combustion zone 17. Although not shown, the combustion reactants preferably include, a flame gas, an additional combustion gas, and a shield gas. Typically, the flame gas is a mixture of methane and oxygen, the combustion gas is additional oxygen, and the shield gas is an inert gas such as nitrogen. It will be understood however,



that other gases and combination of gases can be used for the combustion reactants delivered through burner assembly 12. Flow control mechanism 26 is positioned to provide flow of evaporative liquid 34 into conduit 20.

Evaporative liquid 34 is pumped via pump 24 through flow meter 22 to control  
5 the flow rate of evaporative liquid 34 to injector 14. Evaporative liquid 34 is discharged by injector 14 from burner assembly 12 as atomized liquid droplets 18 into combustion zone 17. During the start-up phase of the present invention, evaporative liquid 34 initially trickles or sputters out of burner  
10 assembly 12 due to initial low pressure and the corresponding low flow rate in conduit 20. However, once the flow rate through conduit 20 is increased by pump 24, evaporative liquid 34 is uniformly delivered into combustion zone 17 as atomized liquid droplets 18, which are quickly combusted in combustion zone 16 without leaving significant solids behind to plug burner assembly 12.

Once a steady state liquid flow rate is attained (i.e., a flow rate at which  
15 transitioning can occur without significant build-up occurring caused by solidification of liquid reactant), flow control mechanism 26 transitions liquid flow from evaporative liquid 34 to liquid reactant 30. In a preferred embodiment, a steady state liquid flow rate is a flow rate substantially equal to that employed during soot deposition and achieved within the conduit prior to  
20 the transitioning step. As flow of liquid reactant 30 is increased, flow of evaporative liquid 34 is decreased, thus a "bumpless" transition occurs. The term "bumpless" as defined herein, means that there are no gaps between the liquids delivered through conduit 20. Instead, the flow rate through conduit 20, burner assembly 12, and into combustion zone 17, remains constant during  
25 transition. Shortly after flow into conduit 20 is exclusively liquid reactant 30, evaporative liquid 34 remaining within conduit 20 is discharged into combustion zone 17 followed immediately by liquid reactant 30 which is combusted to form soot. Burner assembly 12 is directed toward rotating mandrel 36 and soot 38 is deposited on rotating mandrel 36. Although soot 38 is shown in FIG. 1 as  
30 being deposited on rotating mandrel 36 by traversing burner assembly 12 back and forth along the exterior length of rotating mandrel 36, soot deposition can

be achieved by alternative methods, e.g. by moving the mandrel back and forth with respect to the burner assembly.

Once the desired quantity of soot is deposited on rotating mandrel 36, liquid flow is transitioned from liquid reactant 30 to evaporative liquid 34 via flow control mechanism 26. Burner assembly 12 is preferably directed away from rotating mandrel 26 so that when the remainder of liquid reactant 30 in conduit 20 is delivered to combustion zone 17 evaporative liquid 34 discharged immediately thereafter is combusted away from rotating mandrel 36. Flow control mechanism 26 is can then be engaged to prevent all liquid flow into conduit 20. Once the remainder of evaporative liquid 34 in conduit 20 is delivered through burner assembly 12 to combustion zone 17, the trickle flow from injector 14 evaporates cleanly and the burner assembly flame is turned off. Since evaporative liquid 34 is the last liquid discharged from burner assembly 12, there is no liquid reactant 30 available to react with water in the air to form solids in the orifices (not shown) of burner assembly 12 or in conduit 20 adjacent burner assembly 12. Accordingly, cleaning of burner assembly 12 is not necessary prior to additional runs of the liquid delivery system 10 of the present invention.

A second preferred embodiment of the system and method for delivering liquid reactants 40 is schematically depicted in FIG. 2. The second preferred embodiment is particularly well suited for the delivery of one or more dopants, either independently of, or together with other liquid reactants. It will be understood by those skilled in the art, however, that dopants can also be delivered using the first preferred embodiment of the system and method of the present invention 10. When delivered using liquid reactant delivery system 10, dopants can be mixed with liquid reactants 30 in a single reservoir to form a liquid reactant having the desired proportions of liquid reactants 30 and dopants. The liquid reactant can then be delivered in a single step to the combustion zone where it is reacted to form uniformly doped soot. In this way, the soot can be formed without a separate doping step. As will be described in detail below, there are practical and economical advantages to delivering dopants using the second preferred embodiment of the present invention,

particularly when the optical properties of the fiber to be formed are to be altered during laydown.

Liquid reactant delivery system 40 includes a burner assembly 42 having an injector 44. It also includes a liquid reactant reservoir 64 and an evaporative liquid reservoir 68 containing, respectively, liquid reactant 62 and evaporative liquid 66. Like the first embodiment of the present invention, evaporative liquid 66 and liquid reactant 62 are selectively delivered through conduit 60 to injector 44 via flow control mechanism 70. Pump 72 and flow meter 74 control the flow rate of the selected liquid through conduit 60.

In addition, liquid reactant delivery system 40 includes an enclosure 50, an inert gas source 56, a syringe pump 78, and an additional flow control mechanism 76. Like flow control mechanism 70, additional flow control mechanism 76 is preferably a 3-way valve capable of transitioning liquid flow into conduit 60 among a number of liquid sources. One preferred syringe pump 78 is the "Harvard Syringe Pump", model #44, manufactured by Harvard Inc. of Holliston, Massachusetts. Although other delivery devices would be acceptable alternatives, syringe pump 78 includes a syringe 80 and metering device 82 that are particularly well suited for delivering materials in precise quantities. This makes syringe pump 78 ideal for delivering dopants for use in the manufacture of optical waveguides. Inert gas source 56 is preferably a dispenser capable of delivering an inert gas 54 into enclosure 50 through passageway 58.

Liquid reactant reservoir 64, evaporative liquid reservoir 68, and preferably syringe pump 78, are all housed or staged within enclosure 50. Inert gas 54 is delivered through passageway 58 into enclosure 50 to displace all water residing therein and thereby create a dry environment 52. As used herein, the term "dry environment" means an environment essentially free of water, i.e., less than an amount of water which would have an adverse effect on the liquid reactant(s) contained within the reservoir(s). Although not required, it is preferred that inert gas 54 be continuously fed into and exhausted from enclosure 50. Among other benefits, continuously delivering inert gas 54 into enclosure 50 prevents water containing air from entering

enclosure 50 if a leak develops therein. Dry environment 52 provides ideal conditions for working with liquid reactant 62 and dopant 84. Because there is essentially no water within the enclosure 50 when it is provided with inert gas 54, solidification of liquid reactant 62 and dopant 84 is avoided. Although  
5 enclosure 50 can be any size, it is preferably a glove box provided with a pair of arm length rubber gloves which enable an operator of liquid reactant delivery system 40 to access the various liquids staged therein. In this way, the operator can change the solutions to deliver a different liquid reactant 62 and/or dopant 84 as desired without exposing liquid reactant 62 and dopant 84  
10 to water. Accordingly, solutions can be changed between runs without having to clean and/or purge the system. Syringe pump 78 offers the additional advantage of having interchangeable syringe 80. Thus, several syringes 80 containing different dopants 84 can be pre-positioned within enclosure 50 so that numerous runs can be made before additional dopants 84 must be  
15 introduced and staged within enclosure 50.

In one embodiment, inert gas 54, such as argon, helium or dry air (comprising approximately 75% nitrogen and 25% oxygen, but no water), but preferably nitrogen, is introduced into enclosure 50 to create dry environment 52 therein. Liquid reactant 62, and if desired dopant 84 are staged within  
20 enclosure 50 for subsequent delivery through injector 44 of burner assembly 42. Evaporative liquid 66 is also typically housed within enclosure 50 so that it does not absorb water from the air outside of the enclosure, but can be maintained outside of enclosure 50, provided it is not exposed to air or other water sources. After combustion reactants (not shown) are delivered to burner  
25 assembly 42 to create flame 46 at combustion zone 47, flow control mechanism 70 is positioned to deliver evaporative liquid 66 into conduit 60. Evaporative liquid 66 is metered through pump 72 and flow meter 74 to additional flow control mechanisms 76, which passes evaporative liquid 66 to injector 44 and into combustion zone 47 as atomized liquid droplets 48. Once  
30 steady state flow of evaporative liquid 66 is attained, flow control mechanism 70 is engaged to transition flow to liquid reactant 62. Again, the transition is "bumpless", and once the evaporative liquid 66 has cleared from conduit 60,

burner assembly 42 is directed toward rotating mandrel 86. Liquid reactant 62 is discharged from burner assembly 42 as atomized liquid droplets 48 which are reacted in combustion zone 47 to form soot 88 which is deposited on rotating mandrel 86. When desired, dopant 84 can be selectively metered through conduit 60 via additional flow control mechanism 76 and into combustion zone 47 to produce doped soot.

Once the desired quantity of soot 88 is deposited on rotating mandrel 86, burner assembly 42 is directed away from rotating mandrel 86 and liquid flow into conduit 60 is transitioned to evaporative liquid 68 via flow control mechanism 70. Once liquid reactant 62 has cleared conduit 60, flow of evaporative liquid 66 is terminated and the combustion flame 46 is turned off. Because evaporative liquid 66 is the last liquid to exit burner assembly 42, the trickled liquid merely evaporates and no reactant is present in burner assembly 42 for reaction to solids. Thus, plugging the burner assembly 42 and conduit 60 adjacent burner assembly 42 is avoided.

In both the first and second preferred embodiments of the present invention, a preferred liquid reactant 30, 62 for delivery through liquid reactant delivery system 10 and 40, respectively, is a silicon alkoxide such as tetraethoxysilane or tetramethoxysilane. More preferably, liquid reactant 30, 62 is a metal alkoxide such as titanium (IV) propoxide, germanium (IV) ethoxide, potassium butoxide (made soluble with a suitable organic solvent, such as ethylene glycol monomethylether) and other metal alkoxides known in the art. Most preferably liquid reactant 30, 62 is a siloxane, and specifically an organosiloxane such as octamethylcyclotetrasiloxane. It will be understood by those skilled in the art, however, that liquid reactant 30, 62 can be combinations of the above-listed compounds, made soluble with a suitable organic solvent, such as ethylene glycol monomethylether.

The preferred dopants 84 delivered by syringe pump 78 of liquid reactant delivery system 40 are ketonates, alkoxides, acetates,  $\beta$ -diketonates, or fluoro- $\beta$ -diketonates of praseodymium, holmium, and thulium dissolved in a suitable organic solvent such as ethylene glycol monomethylether. The most preferred dopant 84, however, is erbium, which is preferably delivered in liquid

solution as a  $\beta$ -diketonate or fluoro- $\beta$ -diketonate. It will be understood by those skilled in the art that other rare earth elements, as well as other elements having properties beneficial for optical waveguides can be delivered by syringe pump 78. Although not shown in liquid reactant delivery system 10 of FIG. 1, it will also be understood by those skilled in the art that the above-mentioned elements can also be delivered through liquid reactant delivery system 10 using a syringe pump or other suitable delivery device, provided the selected dopant solution is not exposed to water.

Evaporative liquid 34, 66 delivered through liquid reactant delivery system 10 and liquid reactant delivery system 40, respectively, can be organic nitrogen-containing solutions such as amides, amines, and nitriles, but are more preferably organic oxygen-containing solutions. Ketones such as acetone, acetates such as ethylacetate, ethers such as diethylether, and glycols such as ethylene glycol and ethylene glycol monomethylether are representative examples of such organic oxygen-containing solutions. More preferably, alcohol such as ethanol, methanol and propanol are the organic oxygen-containing solutions delivered as evaporative liquids 34 and 66, with ethanol and 1-propanol being the most preferred solutions.

It will be apparent to those skilled in the art that several of the organic oxygen-containing liquids and organic nitrogen-containing liquids described above can be mixed with organosiloxanes, metal alkoxides, siloxanes, silicon alkoxides, metal acetates, metal  $\beta$ -diketonates, metal ketonates, rare earth acetates, ketonates, alkoxides,  $\beta$ -diketonates and/or fluoro- $\beta$ -diketonates, in a single reservoir, for delivery as liquid reactants 30 and 62. When combusted, these solutions form various silicon-oxide and metal-oxide soots that can be captured and used to form optical waveguides having distinct properties. Examples of such organic oxygen-containing liquids are ketones, alcohols, glycols, esters,  $\beta$ -diketones, and carboxylic acids. Examples of such organic nitrogen-containing liquids are amides, amines, nitriles and imines.

It will be apparent to those skilled in the art that various modifications and variations can be made in the system and method for plug-free delivery of liquid reactants through a burner assembly of the present invention without

departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents. In addition, the corresponding structures, materials, acts and  
5 equivalents of all means or step plus function elements in the claims below are intended to include any structure, material, or acts for performing the function in combination with other claimed elements as specifically claimed herein.

**We claim:**

1. A method of forming soot for use in the manufacture of glass while maintaining a plug free liquid delivery system, said method comprising the steps of:
  - a) selectively delivering an alkoxide liquid reactant and a nonatomized evaporative liquid to a combustion zone through a common conduit;
  - b) transitioning between said liquid reactant and said evaporative liquid during said selectively delivering step; and
  - c) reacting said liquid reactant in said combustion zone to form the soot.
2. The method as claimed in claim 1 further comprising the step of:
  - d) evaporating said evaporative liquid in said combustion zone during transient flow conditions.
3. The method as claimed in claim 1 wherein step c) comprises the step of simultaneously decreasing flow of said evaporative liquid while increasing flow of said liquid reactant.
4. The method as claimed in claim 1 wherein step c) comprises the step of simultaneously increasing flow of said liquid reactant while decreasing flow of said evaporative liquid.
5. The method as claimed in claim 3 wherein the step of decreasing flow of said evaporative liquid while increasing flow of said liquid reactant includes the step of activating a valve.
6. The method as claimed in claim 1 wherein step a) includes the step of selectively delivering said liquid reactant and said evaporative liquid through an atomizing burner assembly connected to said conduit.



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14. The method as claimed in claim 12 wherein said inert gas comprises nitrogen.
15. The method as claimed in claim 12 wherein said inert gas comprises argon.
16. The method as claimed in claim 1 wherein the transitioning step occurs during steady state liquid flow.
17. A method of depositing soot to make a glass preform for optical fibers in accordance with claim 1 wherein step d) comprises forming a preform from said soot.
18. The method as claimed in claim 17 further comprising the step of delivering a dopant into said combustion zone through said conduit to create doped soot.
19. The method as claimed in claim 18 wherein said dopant comprises erbium.
20. A liquid delivery system for creating soot in a combustion zone, said system comprising:
  - an alkoxide liquid reactant;
  - an organic evaporative liquid;
  - a burner assembly constructed and arranged to discharge said liquid reactant and said evaporative liquid into the combustion zone;
  - a conduit extending upstream of said burner assembly and adapted to selectively deliver said liquid reactant and said evaporative liquid to said burner assembly; and
  - means for transitioning between said liquid reactant and said evaporative liquid within said conduit.

21. The system as claimed in claim 20 further comprising an enclosure constructed and arranged to house said liquid reactant and said evaporative liquid.

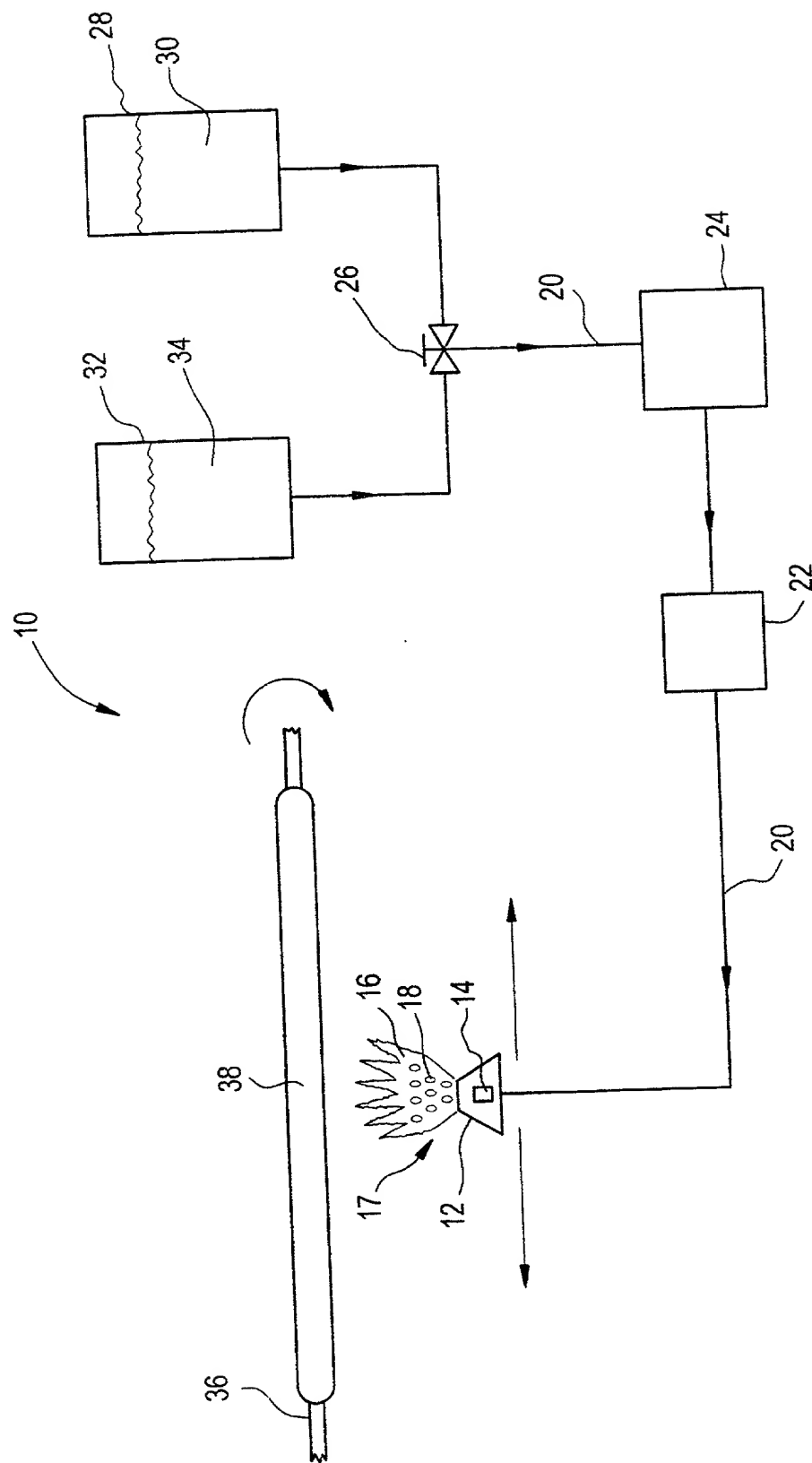
5 22. The system as claimed in claim 21 wherein said enclosure is selectively provided with an inert gas atmosphere to form an environment essentially free of water.

10 23. The system as claimed in claim 22 wherein said inert gas comprises nitrogen.

15 24. The system as claimed in claim 20 wherein said liquid reactant comprises a glass precursor capable of making glass soot used to manufacture preforms for optical waveguide fibers.

20 25. The system as claimed in claim 20 wherein said means for transitioning between said liquid reactant and said evaporative liquid comprises a valve.

FIG.1





As a below named inventor, I declare that:

My residence, Post Office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **SYSTEM AND METHOD FOR PLUS FREE DELIVERY OF LIQUID REACTANTS THROUGH A BURNER ASSEMBLY TO FORM SOOT FOR THE MANUFACTURE OF GLASS**, the specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate, on the same subject matter, having a filing date before that of the application on which priority is claimed:

☐ Country: \_\_\_\_\_ Application No.: \_\_\_\_\_ Filing Date: \_\_\_\_\_

☒ NONE

I hereby claim the benefit under Title 35 United States Code §119(e) and §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37 Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

☒ Provisional No.: 60/095735 Filed: August 7, 1998 Status: (Pending)

☐ Application No. (if a continuation): Filed: Status:

☐ NONE

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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